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ADSORPTION MOBILITY AND ORGANIZATION OF ORGANIC  
MOLECULES AT CLAY SURFACE. (U) KATHOLIEKE UNIV LEUVEN  
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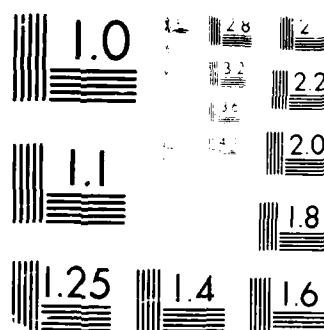
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### *Introduction.*

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The study of clay colloids by means of luminescent probes started a few years ago, in this laboratory. Especially the adsorption of organic molecules on the clay surface is a point of great interest, in order to understand the catalytic properties of these surfaces on various chemical reactions.

A clay surface is negatively charged. Therefore a positively charged pyrene derivative, 3-(1-pyrenyl)-propyltrimethylammonium bromide (PN<sup>+</sup>) is used as fluorescent probe. This molecule is readily adsorbed at the clay surface, simply by adding the probe to a clay suspension.

### *Excimer formation at the clay surface.*

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After adsorption the fluorescence spectra reveals an excimer fluorescence, even when the concentration of PN is very low. The excimers observed on the clay surface are however not formed by diffusion of the PN molecules to each other. Excitation spectra of the excimer emission indicate the existence of interactions between the PN molecules in the ground state. The absence of a growing-in in the fluorescence decay of the excimers also shows the absence of diffusion prior to excimer formation. This means that already in the ground state the PN molecules, or at least a part of the PN molecules, are located next to each other. After excitation, the excimers are formed in an immediate way, maybe after some rotation of the alkyl chain. The fact that these observations are made at very low concentrations of PN (less than 1 % of the C.E.C. ) indicates a non homogeneous distribution of the adsorbed molecules on the clay surface.

*Excimer formation as tool to study other properties of the adsorption on clay particles.*

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This excimer fluorescence seems to be a useful tool to study other properties of the clay colloids. For a clay particle in suspension, one makes a distinction between the external surface and the interlamellar surface. The existence of these two surfaces is the consequence of the fact that, generally spoken, the individual clay platelets aggregate in suspension. The clay surface between the clay platelets is called the interlamellar surface. The aggregation behaviour of the clay platelets in suspension depends on the type of clay. Until now, three different clays are studied. Barasym, a synthetic montmorillonite, Hectorite and Laponite, a synthetic Hectorite. In suspension Barasym has only an external surface available for adsorption, while Hectorite has a large interlamellar surface. Laponite has the interesting feature that the clay particles are individual clay platelets. However an aggregation can be induced by adding  $\text{Ca}^{+2}$  to the suspension. When, for Laponite, the excimer formation is studied as a function of increasing  $\text{Ca}^{+2}$  concentration, a decrease of the excimer formation is observed. This can be explained by a less efficient excimer formation when the aggregation of the clay platelets increases. The PN molecules adsorbed in the interlamellar space will have a restricted mobility, because the distance between the clay platelets does not allow free movement of PN. This explanation is confirmed by the observation of a lot of excimer on Barasym while Hectorite shows less excimer formation. This is due to the fact that with Barasym all the PN molecules are adsorbed at the external surface while with Hectorite a great part of the molecules are adsorbed at the interlamellar surface.

This excimer fluorescence also made it possible to study the adsorption of PN molecules as a function of time. Due to the low concentration of PN in the exchange solution, excimer formation only occurs after adsorption on the clay surface. Thus, by following the steady state intensity of the excimer fluorescence as a function of time an idea about the adsorption and redistribution rate can be obtained. An important characteristic is the immediate observation of excimer emission within the time scale of our experiment (seconds). This indicates a fast adsorption upon adding the PN molecules to a clay suspension. Such an immediate adsorption is observed for all types of clay used in our experiments. In general, the excimer fluorescence decreases as a function of time. The time dependence depends on the type of clay and the type of exchangeable cation. For  $\text{Ca}^{+2}$  exchanged Laponite, the excimer fluorescence intensity at time zero after adsorption increases proportionally to the  $\text{Ca}^{+2}$  content. The excimer fluorescence decreases with time and the rate of decrease is also proportional to the  $\text{Ca}^{+2}$ . For Barasym the time dependence is small while for Hectorite the time dependence can be compared with the one for Laponite in the presence of  $\text{Ca}^{+2}$  ions. To explain these results, the following adsorption model is proposed. Upon addition of the PN molecules to a clay suspension, an immediate adsorption occurs on the external surface of the clay particles. The second molecule, which comes in, will be adsorbed preferentially next to the first one because of preferred Van Der Waals interaction between both. This explains the very efficient excimer formation at the clay surface. With increasing  $\text{Ca}^{+2}$  concentration the clay particles aggregate and the available surface diminishes. The local concentration of PN, and therefore the excimer fluorescence, increases in the adsorption step. The decrease of the excimer fluorescence with time is explained by a redistribution of adsorbed PN molecules from the external to the interlamellar surface. This

decrease is more pronounced in the presence of  $\text{Ca}^{+2}$  because of the reduced mobility of PN in the interlamellar space of the bilayer hydrate. In the case of Barasym only part of the clay platelets have their interlamellar space available for redistribution of PN molecules. This explains the less pronounced decrease of the excimer fluorescence with time. Hectorite behaves as a  $\text{Ca}^{+2}$  Laponite because the external surface of Hectorite is the same as that of an aggregated Laponite.

*Influence of detergent molecules on the adsorbed PN molecules.*

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When Cetyltrimethylammonium chloride (CTAC) is coadsorbed at the clay surface the excimer fluorescence diminishes with increasing detergent concentration. Also, after addition of CTAC, the fluorescence spectrum of PN resembles that of 1-substituted pyrene derivatives solubilized in apolar solvents. This indicates a different environment for PN in the presence of detergent molecules. The polar detergent molecules will form clusters on the clay surface. The pyrene derivative, with the hydrophobic chromophore, will now reside preferentially in such a detergent cluster. Within these clusters the distribution of PN is more homogeneous and the probability that two pyrene derivatives are in close contact to each other decreases, resulting in a decrease of the excimer fluorescence.

The influence of detergent molecules on the distribution of PN molecules on the clay surface, depends very much on the chain length. Below a critical chain length no influence is observed. For PN the critical chain length amounts to 6-8. This is explained in the following way. When the chain length of the detergent is smaller than the length of PN, the latter will not be solubilized in the detergent cluster. The pyrene chromophore would still

reside in the water phase. Therefore the PN molecules form separate clusters as if no detergent is present. An additional proof for this so called critical chain length is performed with another probe available in the laboratory, 1-pyrenyltrimethylammonium chloride. For PN, hexyltrimethylammonium chloride is unable to influence the distribution of adsorbed PN molecules, resulting in no decrease of the excimer fluorescence. 1-pyrenyltrimethylammonium chloride does not form excimers after adsorption on the clay surface. It does however form ground state complexes, noticed in absorption and excitation spectra. Again this indicates a non homogeneous distribution of the adsorbed probes on the clay surface. When hexyltrimethylammonium chloride is coadsorbed the formation of ground state complexes is lowered. This proves that the chain length of the detergent must match the length of the probe. For PN a length of six is too small while for 1-pyrenyltrimethylammonium chloride the length is sufficient. Recently, the influence of detergents with two apolar tails on the adsorption of PN has been studied. Some measurements have been done with didodecyldimethylammonium chloride (DDAC). It seems that the influence of DDAC on the distribution of PN molecules is more pronounced compared with a detergent with only one apolar tail. Only a slight amount of DDAC must be added to inhibit excimer formation on the clay surface. Further measurements are in progress to understand the mechanism of the detergent action.

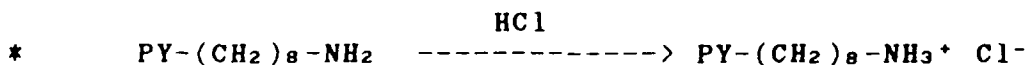
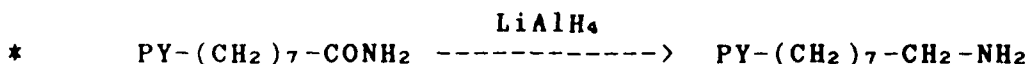
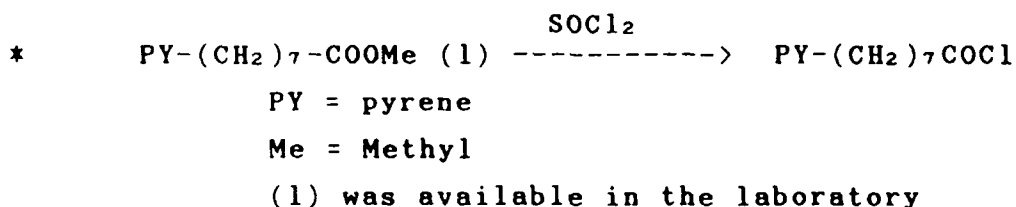
*Time resolved fluorescence decay analysis*

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For PN adsorbed on a clay surface some fluorescence decay analysis are performed. Even in the presence of enough detergent, in order to avoid excimer formation, a



complex decay is observed which could be fitted to different functions. The best fit was obtained with a two-exponential function. A short decay time is always observed in these fluorescence decays. The cause of these short decay times could be the clay surface. Therefore three different probes, with a different chain length, will be studied. Two of them are already mentioned : 3-(1-pyrenyl)propylammonium chloride and 1-pyrenyl-trimethylammonium chloride. Another probe with a longer chain length has recently been synthesized: 8-(1-pyrenyl)-octylammonium chloride. The synthesis can be depicted as follows:



By using these three different probes we will try to gain more information about the orientation of the adsorbed molecules, especially at low coverages and about the influence of the clay surface on the photophysical properties. Especially at low coverages there is no indication until now how the adsorbed molecules are oriented on the surface. If one assumes that the quenching, seen in the fluorescence decay, is caused by the clay surface, this quenching must be different for the different probes, when they are oriented perpendicular to the surface. Otherwise, one can assume a

flat orientation . Also an attempt will be made to study the influence of coadsorbed detergent molecules on the orientation of the probe. Once the influence of the clay surface on the decay times has been wiped out a detailed quenching study can be performed in order to obtain more information about the diffusion on the surface, the accessibility of adsorbed probes, the diffusion and aggregation of the clay particles

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